Photoemission Studies of Semiconductor Nanocrystals

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INTRODUCTION

Semiconductor nanocrystals have been the focus of much attention in the last ten years due predominantly to their size dependent optical properties. Namely, the band gap of nanocrystals exhibits a shift to higher energy with decreasing size due to quantum confinement effects. Figure 1 shows this shift of the onset of absorption of CdSe nanocrystals. Research in this field has employed primarily optical techniques to study nanocrystals, and in this respect this system has been investigated extensively. In addition, we are able to synthesize monodisperse, crystalline particles of CdS, CdSe, Si, InP, InAs, as well as CdS/HgS/CdS and CdSe/CdS composites. However, optical spectroscopies have proven ambiguous in determining the degree to which electronic excitations are interior or surface admixtures or giving a complete picture of the density of states. Photoemission is a useful technique for understanding the electronic structure of nanocrystals and the effects of quantum confinement, chemical environments of the nanocrystals, and surface coverages. Of particular interest to us is the surface composition and structure of these particles, for we have found that much of the behavior of nanocrystals is governed by their surface [1,2]. Previously, we had performed x-ray photoelectron spectroscopy (XPS) on CdSe nanocrystals [3,4]. XPS has proven to be a powerful tool in that it allows one to determine the composition of the nanocrystal surface. Specifically, we were able to investigate the coverages of capping groups on the surface of the nanocrystals, effects of oxidation, and the

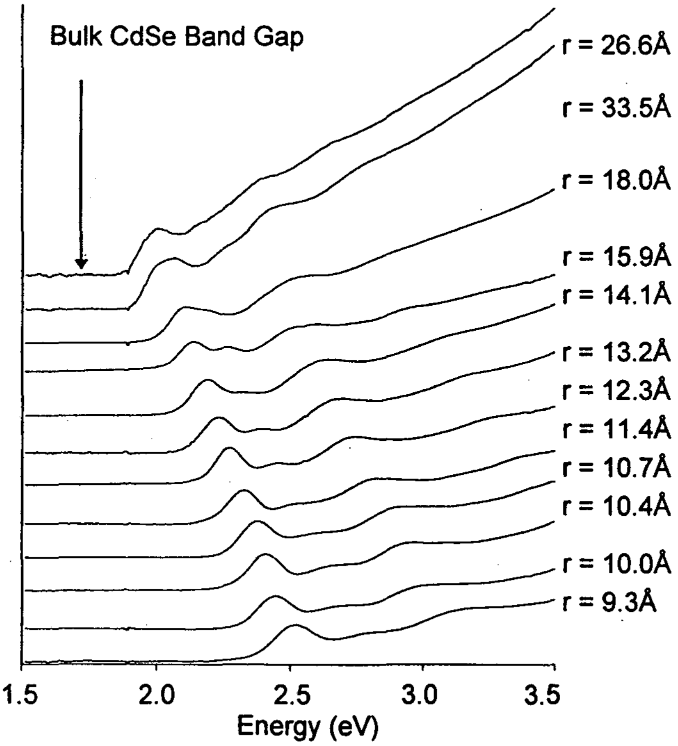

Figure 1: Optical absorption spectra of several sizes of CdSe nanocrystals.

influence of varying chemical environments by examining core level peaks and their chemical shifts.

Currently, we are employing photoemission to a further extent in order to study size effects on core level lineshape and valence band density of states. Much of this work is currently in progress both on-line as well as off-line.

EXPERIMENTAL

Recently, photoemission studies of semiconductor nanocrystals was made possible by the implementation of a novel synthetic technique [5]. Hexanedithiol chains are used as organic linkers between the nanocrystals and a metal substrate. First, these organic chains are allowed to self-assemble onto a gold layer. The samples are then placed into a nanocrystal solution which is stirred for a long period of time, allowing the crystallites to attach themselves to the exposed end of the organic chain. These organic layers make an electrical contact to nanocrystals because they provide a short pathway of approximately 10Å in length through which electrons can tunnel from a conducting substrate. Since in this form the nanocrystals do not charge, the samples are suitable for electronic spectroscopies such as photoemission.

For both studies, the photoemission experiment was performed in a ESCA chamber with a base pressure of 5×10^{-10} torr. The radiation source was either a conventional Mg anode (Kα) or synchrotron radiation from beamline 6.3.2 (bend magnet) in the range of 50-500eV. Photoelectrons were detected in a hemispherical electron energy analyzer which had a resolution of 25 meV. Ultimate resolution was determined by the radiation source, which was 695 meV for the Mg anode and ~100meV for the synchrotron beam.

INVESTIGATIONS OF CORE LINEWIDTHS AND BINDING ENERGY VERSUS SIZE

By examining the linewidths of peaks in the photoelectron spectrum, we would obtain information on the intrinsic lifetimes of charge carriers in nanocrystals. The excited photoelectron state can decay in several ways, radiatively by x-ray emission or nonradiatively by Auger or other processes. Furthermore, we speculate that these lifetimes are strongly influenced by the size of the particle: a hole created in the photoelectron process can be quenched more rapidly in larger particles due to increased interatomic electronic relaxation, or screening. We have the means to alter the size of our particles systematically, therefore we can study the hole lifetime as a function of nanocrystal size. Previously, we were unable to analyze linewidths of photoelectron peaks because the resolution of an ESCA system is limited largely by its x-ray source. Standard x-ray anodes (Mg, Al) have a resolution of approximately 750 meV, while it is estimated that intrinsic linewidths of peaks are comparable or less. Consequently, these sources are not suitable for examining lifetimes and a higher resolution light source is necessary. We can synthesize CdSe and InAs particles from 20Å to 60Å in diameter, with a size distribution as narrow as 1.5Å. Therefore, these particles are most suitable for examining the widths of the Cd and Se 3d cores of CdSe or the In 3d and As 2p cores of InAs.

The hole screening also has an effect on the core level energy. Studies on gas phase Ar clusters by Möller and co-workers show that this size-dependent hole screening shifts the binding energy of the Ar 2p level to higher energies with decreasing cluster size [6]. We have been working towards observing such an effect in our nanocrystals.

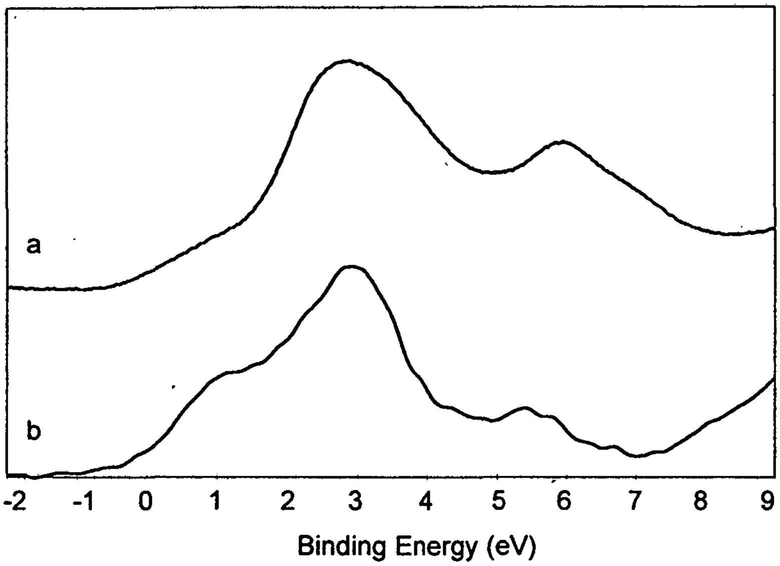

Figure 2. a.) Valence band spectrum obtained from CdSe nanocrystals on dithiol / Au substrate. b.) Spectrum obtained by subtracting dithiol / Au background.

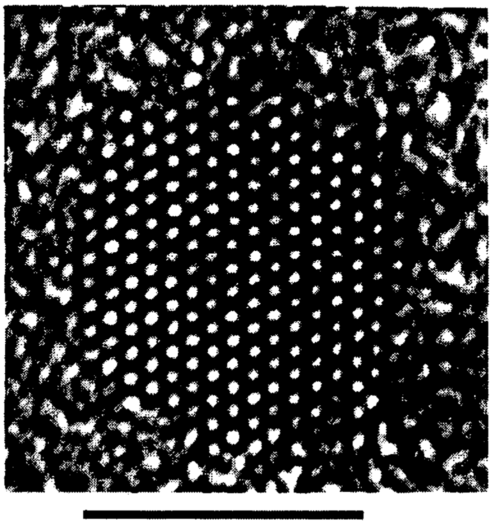

Figure 3. High Resolution TEM of CdSe nanocrystal. The bar indicates a length of 50Å.

INVESTIGATION OF VALENCE BANDS VERSUS SIZE

We are also utilizing x-ray and ultraviolet photoemission experiments to study the valence band as a function of size of the particle [7]. As the size of the nanocrystal is decreased, the valence band shifts to higher binding energy. We are interested in obtaining the density of states (DOS) in both the valence and conduction bands and seeing how they evolve as a function of the size of the nanocrystal. Optical spectroscopy is limited to examining only the gap between the valence and conduction bands within constrictions of selection rules. Photoelectron spectroscopy, however, enables one to obtain a picture of the entire valence band. In our experiments on the beam as well as off-line, we have determined a method to obtain the valence DOS of CdSe and InAs nanocrystals without the DOS from the substrate (the hexanedithiol on Au). Figure 2a shows a valence band taken of CdSe nanocrystals on a hexanedithiol substrate. The spectra in 2b is obtained by subtracting the hexanedithiol on Au background, therefore it is characteristic of the CdSe nanocrystal only. We have repeated this experiment on other substrates (for example, indium tin oxide, ITO) to confirm that this spectrum is of the nanocrystals. Thus far we have been able to do so using a conventional x-ray source, which has a resolution that obscures any size effects of the nanocrystals. We are interested in how the valence DOS evolves with the size of the particle, and seeing if it exhibits predicted 0-D behavior. If it were possible to isolate the surface DOS [8] it would be interesting to watch its evolution with size of the nanocrystal. For example, does the surface DOS reflect the approximate surface to volume ratios for a given size quantum dot? Where does it lie in energy relative to the band gap? As aforementioned, we have the chemical ability to alter the surface of the particle and thus look at which states in the valence band are affected. Another interesting property that can be obtained by UPS is the way the valence energy levels of the nanocrystal line up with the substrate Fermi level [9]. What is the offset between the Au Fermi level and the top of the valence band in CdSe? Is there band bending? These questions are necessary for the understanding of transport in these systems, and currently we are working in collaboration with the McEuen group to understand the behavior of this system [10].

ORIENTED CRYSTALLITES AND PHOTOELECTRON DIFFRACTION

Current work is underway to orient a monolayer of nanocrystals on a plane. Many [11, 12, 13] have devised novel methods to align particles on substrates such that their optical axes are oriented in a single direction relative to the plane. The nanocrystals on our self assembled monolayer samples are randomly oriented, thus their photoelectron spectra represent an averaging over a random distribution. With aligned particles we would have the potential to perform another order of photoemission experiments that would resolve the question of the nanocrystal's surface. Photoelectron diffraction (XPD) would allow us to determine the both the atomic positions (by scanning in angle) and bond lengths (by scanning in energy) of the surface atoms. Thus it would give us the most complete picture of the surface. Figure 3 shows a high resolution transmission electron micrograph of a CdSe nanocrystal. From the image, we can see the interior lattice structure, which we have determined to be identical to that of bulk CdSe. However, the image tells us nothing about the surface structure, since essentially it is a two-dimensional projection of a nanocrystal. Although we can predict beforehand what surfaces will be more stable than others, we do not know exactly what the surface looks like.

ACKNOWLEDGMENTS

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